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Karl O. Albrecht
Iowa State University

Kyle S. Wagenbach
Iowa State University

Justinus A. Satrio
Iowa State University

See next page for additional authors

Development of a CaO-Based CO_2 Sorbent with Improved Cyclic Stability

Karl O. Albrecht,[†] Kyle S. Wagenbach,[†] Justinus A. Satrio,[‡] Brent H. Shanks,[†] and Thomas D. Wheelock*,[†]

Department of Chemical and Biological Engineering, 2114 Sweeney Hall, and Center for Sustainable Environmental Technologies, 0411 Marston Hall, Iowa State University, Ames, Iowa 50011

The carbonation of CaO is an attractive method for removing CO_2 from hot gas mixtures. However, regeneration and reuse of a CaO-based sorbent causes a gradual decline in absorption capacity, which ultimately limits the life of the material. Various methods have been proposed for increasing the life cycle performance of a CaO-based sorbent. Two of these methods were selected for further investigation. One method incorporates an "inert" material in the sorbent, while a second method stabilizes the sorbent through controlled sintering. Promising results were achieved with both methods when they were applied separately to a sorbent derived from a natural limestone. In one case MgO was finely dispersed within the sorbent, where it served as an "inert" material in the sense that it did not absorb CO_2. A concentration of approximately 20 wt % appeared to be nearly optimal. In a second case the sorbent was stabilized by calcining the material at 1100 °C for 5 h. Although neither method produced a completely stable material, the stability of the sorbents was improved sufficiently so that by the end of a 1200-cycle test the absorption capacity of either of the treated sorbents was 45% greater than that of an untreated sorbent and the rate of decline was very small.

Introduction

The carbonation of CaO is a reversible reaction with several potential applications.

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad \Delta H_{25°C} = -175 \text{ kJ/mol} \quad (1)$$

Reaction 1 may be used in the future to absorb CO_2 from hot process streams for subsequent disposal in order to alleviate global climate change.[1,2] CaO has also been demonstrated for selective, in situ CO_2 separation from other reaction products produced in a combined methane reforming/water gas shift reactor resulting in improved feedstock conversion.[3−9] Energy storage systems based on reaction 1 have also been investigated because of the high exothermicity of the carbonation reaction.[10−12] The major challenge associated with some practical applications of reaction 1 is a lack of total reversibility. At any temperature above the equilibrium decomposition temperature, $CaCO_3$ will completely decompose to form CaO. However, upon recarbonation, the reaction will not proceed to completion within a reasonable time. Therefore, upon subsequent regeneration and carbonation, less CO_2 is absorbed and the fraction of CaO recarbonated declines from cycle to cycle.[13,14] When it is impractical to continuously purge and replenish the CaO, such as when it is combined with a catalyst for steam reforming methane, the absorption capacity of the CaO must be maintained over an industrially relevant lifetime.[8,9] Consequently, there is need for a CaO-based sorbent such that its absorption capacity declines only very gradually as it is loaded and regenerated.

One possibility for enhancing the cyclic stability of CaO-based sorbents is through the incorporation of inert materials. MgO has been proposed for this application since it is inert under some conditions where CaO may be used for absorbing CO_2. Dolomite, a mineral which nominally has a 1:1 ratio of $MgCO_3$ to $CaCO_3$, with the Ca and Mg ions interspersed in layers in the naturally occurring crystal, decomposes into separate MgO and CaO phases.[15] The CaO derived from dolomite was found to be more stable than CaO derived from limestone when subjected repeatedly to CO_2 absorption and regeneration.[16,17] Huntite, which has a 1:3 molar ratio of $CaCO_3$ to $MgCO_3$, provided CaO with even greater stability.[17] However, the presence of a large amount of inert material in an industrial sorbent is undesirable since it would increase capital and operating costs. Therefore, in the present investigation consideration was given to the use of smaller concentrations of MgO applied by a doping method.

Other materials have been added to CaO to improve its stability for repeated CO_2 absorption/desorption. Salvador et al.[18] subjected limestone impregnated with 0.5 wt % NaCl to thermogravimetric analysis (TGA) using a temperature of 700 °C for absorption and 850 °C for regeneration. The CaO conversion achieved with a NaCl-doped sample was lower than the conversion achieved with an undoped sample during the first CO_2 absorption cycle. However, after 14 carbonation/calcination cycles, the conversion achieved with a NaCl-doped sample was 40% compared to a CaO conversion of only 30% achieved by an undoped sample after 11 cycles. Aihara et al.[10] doped CaO with inert $CaTiO_3$ either by using an alkoxide method or by physically mixing $CaTiO_3$ with $CaCO_3$. The doped CaO was then tested by employing thermogravimetric analysis at 750 °C. The presence of $CaTiO_3$ was reported to enhance the cyclic stability of the CaO-based sorbent over 10 cycles when compared to CaO without $CaTiO_3$ present. Li et al.[19] investigated the effect of adding an inert phase consisting of $Ca_{12}Al_{14}O_{33}$ to CaO. The $Ca_{12}Al_{14}O_{33}$ phase was created by adding $Al(NO_3)_3 \cdot 9H_2O$ to the sorbent and then calcining the material. Sorbents with the $Ca_{12}Al_{14}O_{33}$ phase present exhibited enhanced stability over 13 cycles. Later work showed that a 25/75 weight ratio of $Ca_{12}Al_{14}O_{33}$ to CaO followed by calcination at 900 °C for 1.5 h was optimal for preparing this sorbent.[20] TGA tests performed with carbonation at 650 °C and calcination at 850 °C showed that after 50 cycles the sorbent was still capable of achieving a CaO conversion of 65%.

Some additives have been shown to be ineffective or even detrimental to the stability of CaO. Lu et al.[21] found no

* To whom correspondence should be addressed. E-mail: wheel@iastate.edu.
[†] Department of Chemical and Biological Engineering.
[‡] Center for Sustainable Environmental Technologies.

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enhancement in CaO stability by the addition of 10−50 wt % silica when the sorbent was tested at 700 °C. The material was prepared by adding silica to a solution of calcium acetate followed by evaporation at 70 °C to precipitate the salt and then calcination at 750 °C. Another investigation showed that the addition of $SrCO_3$ to limestone had a detrimental effect regardless of whether the dry powders were mixed together or coprecipitated from solution.[22] TGA testing showed that after eight cycles a CaO conversion of 44% was achieved with the sorbent prepared from pure limestone, whereas a conversion of only 17−20% was achieved with the sorbent containing strontium. Scanning electron micrographs of the samples with strontium present showed increased sintering and rounding of the particles after eight cycles.

Enhancing the ability of CaO to absorb CO_2 over many cycles can also be achieved through modification of the pore structure.[23] It is well-known that subjecting a microporous material to sintering conditions will coalesce smaller pores into larger pores. Although this will reduce the pore surface area, it can also improve the stability of the material, and it can make the central core of a particle more accessible to the CO_2. Without such treatment the micropores near the surface of a sorbent particle can become plugged by the reaction product before the CO_2 reaches the core. The process is exacerbated by the increase in molar volume which accompanies the conversion of CaO into $CaCO_3$. With the proper balance of micropores and mesopores, more of a sorbent particle should be capable of participating in the absorption process.

Altered pore structures of CaO sorbents have been previously reported. In CO_2 absorption tests conducted by Silaban et al.,[16] higher conversions of CaO in dolomitic lime were attributed in part to excess pore volume created by the initial decomposition of the $MgCO_3$. Hughes et al.[24] increased the pore volume and pore surface area of two different limestone samples by a process of steam hydration conducted at 150 °C and 475 kPa. When the hydrated limestones were subjected to a cyclic absorption test conducted at 750 °C, a CaO conversion of 52% was achieved after 20 cycles. Gupta and Fan[1] reported precipitating $CaCO_3$ by reacting Ca^{2+} ions with CO_3^{2-} ions in water to create a sorbent with pores predominantly in the mesoporous region of 5−20 nm. When the CaO derived from the precipitated calcium carbonate was subjected to an absorption test at 700 °C, a CaO conversion of 95% was obtained after two cycles. The authors claimed that the larger pores that formed were less susceptible to pore plugging than the micropores produced by calcining limestone or dolomite.

Information about the life of a CaO-based sorbent material is difficult to evaluate on the basis of a few initial absorption and regeneration cycles. Grasa and Abanades[25] investigated sorbents derived from different sources of limestone that were then carbonated and regenerated at different process conditions. They discovered that the conversion of CaO during the first 10−25 cycles varied widely depending on the limestone source, regeneration temperature, and partial pressure of CO_2. However, sorbent testing for more than 100 cycles revealed that, regardless of process conditions or limestone type, the absorption capacity of all the samples approached 7.5−8.0 wt %, and the capacity remained constant for up to 500 cycles. For some industrial applications, sorbent capacity must remain in a useful range for thousands of absorption and regeneration cycles. Sorbents with a high initial absorption capacity acquired by a costly treatment process would be of little use if the benefit of the treatment was lost after a few hundred cycles. Many CaO-based sorbents reported in the literature are tested over only tens of cycles, which may not be sufficient to determine whether the sorbent will have a useful life.

Although many methods have been proposed for extending the life cycle performance of a CaO-based sorbent, only a few seem well suited for an economical, industrial process. Among these methods, two were selected for further study. One method makes use of an inert material which is incorporated in the sorbent, while a second method stabilizes the sorbent through controlled sintering. To demonstrate the first method, MgO was selected as an inert material, since it would not absorb CO_2 under the conditions being considered for applying the sorbent. Numerous sorbent samples were prepared subsequently by impregnating ultrafine size limestone particles with $Mg(NO_3)_2$ in various concentrations followed by calcination to decompose the nitrate. To demonstrate the second method, samples of the ultrafine size limestone were calcined under conditions that became increasingly severe resulting in progressively greater stability. The prepared sorbents were then subjected to a life cycle performance test in which the material was repeatedly loaded with CO_2 and regenerated under carefully controlled conditions.

Experimental Methods and Materials

Materials. Different sources of CaO were used in this study. Limestone was obtained from two sources. Columbia River Carbonates in Washington state provided Microna 3 limestone with a mean particle size of 3.2 μm and with a $CaCO_3$ content greater than 97 wt % according to the producer. Coarser limestone with 97 wt % $CaCO_3$ according to the producer was obtained from the Ames, IA, quarry of Martin Marietta Aggregates. This limestone was ground and screened to a size of −212/+63 μm.

Dolomitic limestone, or dolomite, was received from Graymont Dolime (OH), Inc., in Ohio. The dolomite was also ground and screened to a size of −212/+63 μm. Fisher Scientific was the source of the calcium acetate, calcium carbonate, and calcium hydroxide used in sorbent studies. These materials were of reagent grade and were used as received.

Lanthanum nitrate [$La(NO_3)_3 \cdot xH_2O$] and magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] were purchased from Sigma-Aldrich. The magnesium nitrate was of reagent grade. Due to the indeterminate nature of the hydrate in the lanthanum nitrate, a stock solution was prepared. The molarity of the stock solution was then determined gravimetrically by heating samples of a known volume of the stock solution in air to at least 900 °C for 12 h or more to convert the lanthanum nitrate to lanthanum oxide, La_2O_3, which could be weighed.

Preparation Methods. Most sorbents were calcined before undergoing cyclic tests of absorption and regeneration unless otherwise noted as "uncalcined", in which case the material was tested unaltered. For the initial calcination of a sorbent material, a thin layer consisting of about 6 g of material was calcined in a quartz boat in a horizontal tube oven. Calcination at 900 °C began with a 2 h temperature ramp from room temperature to 900 °C followed by an isothermal step at 900 °C for the appropriate time. The calcined material was then cooled to room temperature using a 2 h temperature ramp. For materials calcined at 1100 °C, a 3 h ramp from room temperature was employed followed by an isothermal step for the appropriate time at 1100 °C. The calcined material was then cooled to room temperature using a 2 h ramp. All initial calcinations were performed under flowing air.

For some studies, magnesium nitrate or lanthanum nitrate was added to Microna 3 limestone in an amount designed to provide

an appropriate concentration of either oxide in the calcined sorbent. Both limestones were conservatively assumed to contain 97 wt % $CaCO_3$. The nitrate salt was dissolved in tetrahydrofuran (THF), and an appropriate amount of this solution was added to the Microna 3 to form a thick paste when mixed in a mortar. After mixing, the THF was evaporated, and the resulting powder was dried in the mortar at 120 °C for at least 5 h. The powder was then reground in the mortar and calcined at the appropriate temperatures using the ramping procedures described above. Some sorbent tests were performed using Microna 3 limestone, which had been calcined prior to adding one of the nitrates. The procedure was the same as the preceding one except that the Microna 3 limestone was calcined in flowing air at 750 °C for 5 h before addition of the nitrate. All samples were stored in a desiccator for the time between preparation and characterization.

Characterization Methods. The absorption capacity and the effect of multiple absorption and desorption cycles on the life of the sorbent were determined with a thermogravimetric analysis (TGA) system which utilized a Cahn 2000 electrobalance. The sorbent was tested as a powder contained in a small ceramic, cylindrical cup, which had a diameter of 6 mm and a height of 6 mm. The cup was half-filled with sorbent material, which typically provided a sample mass of 20−40 mg. However, the mass would vary depending on the density of the material. For calcium acetate only 11.2 mg would half fill the cup. For testing the sample was suspended in a vertical quartz tubular reactor having an inside diameter of 25 mm and was subjected to a series of absorption and desorption cycles conducted isothermally at 750 °C and at 1.0 atm. During an absorption step a gas stream composed of 25 vol % CO_2 and 75 vol % N_2 was supplied to the reactor at a rate of 3.72 mmol/min for 20 min. This was followed by a desorption step in which only N_2 was supplied for 30 min at a flow rate of 2.79 mmol/min. The two steps constituted a complete cycle. While these conditions did not produce the high concentration of CO_2 required for an industrial application, they were well suited for experimentally conducting a large number of absorption and regeneration cycles because they did not require varying the temperature throughout each cycle, which would have been very time-consuming overall.

Scanning electron microscopic (SEM) images of the sorbent were collected by using a JEOL 840A SEM. Images were collected using an accelerating voltage of 20 kV and secondary electron imaging. The fresh sorbent samples were imaged after initial calcination at 900 °C for 3 h, and tested sorbent samples were imaged following recarbonation of the samples after the 30th cycle.

The pore volume distribution of selected samples of sorbent material was determined with a Micromeritics ASAP 2020 instrument. The BJH method of desorption analysis was employed in which nitrogen was adsorbed at −196 °C. This method required a larger sample of material than could be treated with the TGA system. Therefore, samples of sorbent material were treated in a heated, horizontal tubular reactor that could accommodate a quartz boat holding about 8 g of material. The samples were treated isothermally at 750 °C by a cyclic process consisting of a 20 min absorption step followed by a 30 min desorption step. A gas mixture consisting of 25 vol % CO_2 and 75 vol % N_2 was supplied at a rate of 9.24 mmol/min for absorption, while only nitrogen was supplied at a rate of 6.93 mmol/min for desorption. The process was interrupted periodically to remove a 0.5 g sample of material for analysis. This was timed so that the sample was collected 5 min before the end of a desorption step.

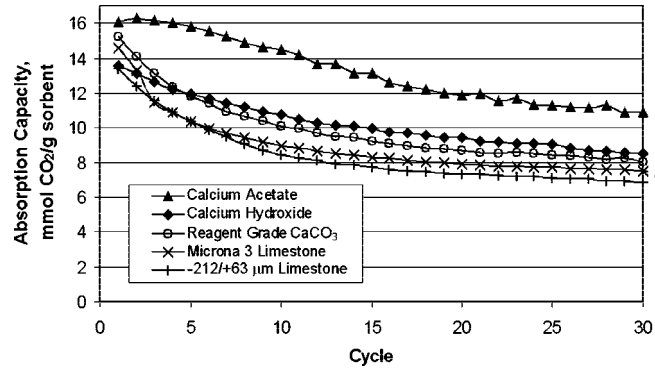

Figure 1. Apparent absorption capacity of CaO prepared by calcining various source materials at 900 °C for 3 h.

Experimental Results and Discussion

Calcium oxide can be prepared from various precursors such as limestone and dolomite. An alternative precursor which has been shown to produce somewhat more stable CaO is calcium acetate.[21] These and several other precursors were utilized to prepare sorbents for evaluation in the present study. After each material had been calcinced at 900 °C for 3 h, it was subjected to a multicycle test of absorption and regeneration conducted at 750 °C. The results of a preliminary series of tests are presented in Figure 1. In this and subsequent figures the CO_2 apparent absorption capacity of the calcined material is indicated. Figure 1 shows that the absorption capacity of each material decreased with usage. The theoretical maximum absorption capacity of the limestone with 97 wt % $CaCO_3$ and 3 wt % inert material is 16.9 mmol of CO_2/g of calcined sorbent. Although CaO derived from calcium acetate displayed the highest absorption capacity, the material was not completely stable. Because of their higher purity, reagent-grade calcium hydroxide and calcium carbonate provided sorbents with a slightly greater absorption capacity than those provided by either limestone. However, the reagent-grade materials were not chosen for further investigation because of their higher cost.

Since Bandi et al.[17] had shown previously that the absorption capacity of CaO was more stable when derived from dolomite or huntite than from limestone, the possibility of stabilizing CaO with smaller concentrations of MgO was investigated by impregnating Microna 3 limestone with $Mg(NO_3)_2$ followed by calcination at 900 °C for 3 h to decompose the nitrate. Sorbents with different levels of MgO were then subjected to 30-cycle tests of absorption and regeneration. The results presented in Figure 2a indicate the variation in absorption capacity of each material identified by the mass ratio of MgO to CaO. The indicated values of the mass ratio of MgO to CaO encompass that of dolomitic lime (0.72 g of MgO/g of CaO). It is apparent that the initial absorption capacity decreased as the MgO content increased, but at the same time the sorbent became more stable so that its capacity decreased less with usage. The decrease in absorption capacity was largely due to the decrease in CaO content of a given sample as the MgO content was increased. The absorption capacity may also have declined because MgO covered the CaO particles. Of special interest is the increase in absorption capacity with usage of the sorbent with 1.0 g of MgO/g of CaO. Such an increase is not well understood, although it was likely due to rearrangement of the pore structure or crystal structure. Another interesting feature suggested by

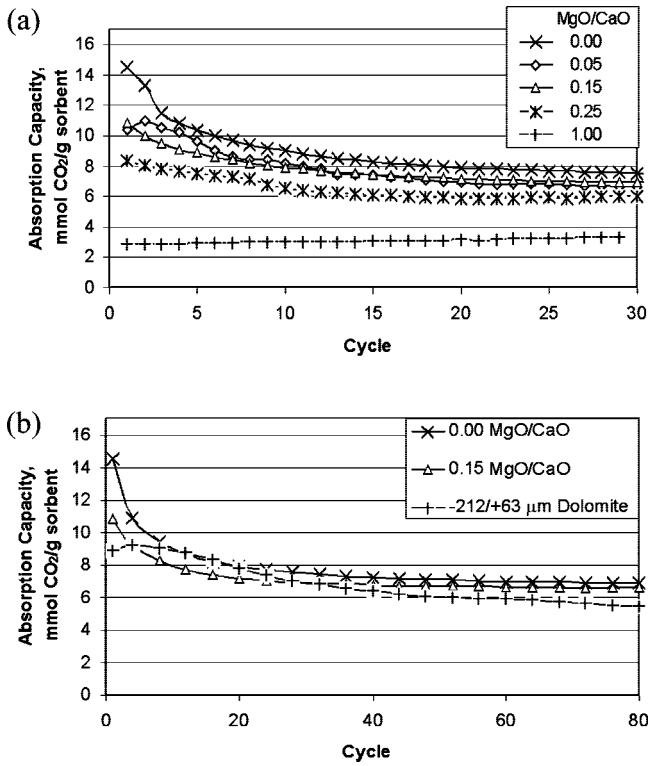

Figure 2. Effect of MgO expressed as g of MgO/g of CaO on apparent absorption characteristics of CaO derived from Microna 3 limestone or dolomite. All samples were initially calcined at 900 °C for 3 h before testing. (a) Effect of different MgO loading levels; (b) effect of extended life cycle testing.

Figure 2a was the apparent activation of the sorbent with 0.05 g of MgO/g of CaO between the first and second cycles. This phenomenon was not observed with any of the other samples doped with MgO.

A longer life cycle test was conducted with several samples, and the results are presented in Figure 2b. Although the initial absorption capacity of the sorbent without MgO present was greater than that of the sorbent with 0.15 g of MgO/g of CaO, both materials absorbed about the same amount of CO_2 at the end of 80 cycles. This result indicates that more of the CaO in the sorbent containing MgO was available for absorption of CO_2. The dolomitic lime absorbed the same amount of CO_2 as the Microna 3 lime between 10 and 20 cycles even though the dolomitic lime was equivalent to a sorbent with 0.72 g of MgO/g of CaO. Thus, more of the CaO in dolomitic lime was available for reaction. Others have attributed such behavior to the increased porosity of the dolomitic lime formed upon calcination.[16]

Another material considered as a potential stabilizing agent for the CaO sorbent was La_2O_3. This material had been shown previously to stabilize alumina when alumina had been used as a catalyst support.[26,27] However, unlike MgO, La_2O_3 cannot be considered completely inert for the conditions used in the present investigation. Shirsat et al.[28] reported that lanthanum dioxycarbonate, $La_2O_2CO_3$, is a stable intermediate in the decomposition of lanthanum carbonate, $La(CO_3)_3$. $La_2O_2CO_3$ decomposes above 720 °C via the reaction

$$La_2O_2CO_3 \leftrightarrow La_2O_3 + CO_2 \quad (2)$$

However, the equilibrium partial pressure of CO_2 for reaction 2 at 750 °C is 0.06 atm. Therefore, the carbonation of La_2O_3 appeared likely. To investigate this possibility, a sorbent derived from Microna 3 limestone was impregnated with lanthanum to

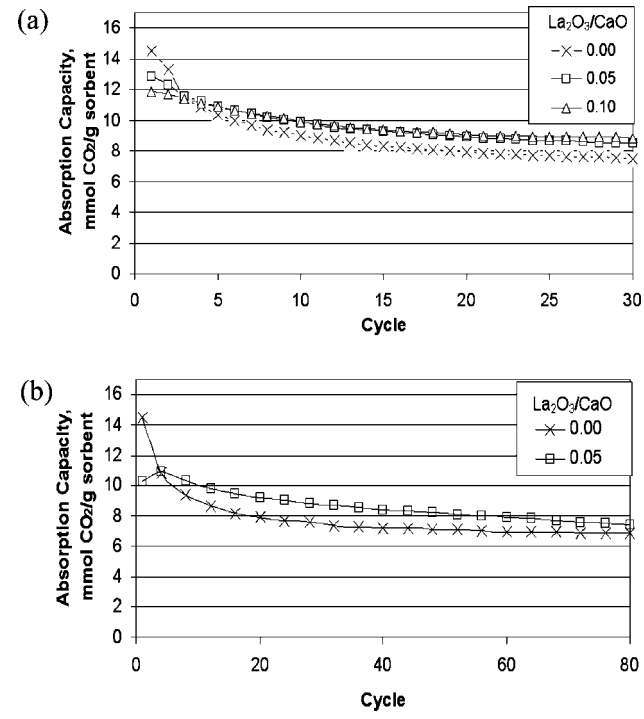

Figure 3. Effect of La_2O_3 expressed as g of La_2O_3/g of CaO on apparent absorption characteristics of CaO derived from Microna 3 limestone. The samples were initially calcined at 900 °C for 3 h before testing. (a) Effect of different La_2O_3 loading levels; (b) effect of extended life cycle testing.

provide a mixture with 0.10 g of La_2O_3/g of CaO. After this material was subjected to a 30-cycle test of CO_2 absorption and regeneration in the TGA, it was analyzed by X-ray diffraction and was found to contain a small amount of crystalline $La_2O_2CO_3$. In order to determine the amount of CO_2 that could be absorbed by La_2O_3, a pure La_2O_3 sample was prepared by calcining $La(NO_3)_3$ at 900 °C for 3 h, and then it was subjected to a four-cycle absorption/regeneration test at 750 °C. It was found that after four cycles less than 0.1 mmol of CO_2/g of sorbent was being absorbed. Therefore, La_2O_3 was not absorbing a large amount of CO_2, but was also not completely inert.

To see what effect La_2O_3 would have on the stability of the sorbent, samples were prepared with different ratios of La_2O_3 to CaO, based on Microna 3 limestone. After the samples had been calcined for 3 h at 900 °C, some were treated to 30 cycles of absorption and regeneration at 750 °C. The results presented in Figure 3a show that the samples containing small amounts of La_2O_3 had a higher absorption capacity through 30 cycles than the sample of untreated limestone. On the other hand, different levels of La_2O_3 had little effect. Extending the sorbent performance to 80 cycles produced the results shown in Figure 3b. It can be seen that as the number of cycles was extended beyond 30, the absorption capacity advantage of the sorbent with La_2O_3 gradually faded and almost disappeared entirely after 80 cycles. Consequently, this is an excellent example of the need for extended testing of CaO sorbents. While it could reasonably be assumed from Figure 3a that the addition of lanthanum is indeed beneficial, further testing showed that the benefit gradually disappeared after many more cycles.

An alternative method of preparing the sorbents with added MgO or La_2O_3 was also investigated. Microna 3 limestone with little initial porosity was calcined at 750 °C for 5 h in air before addition of the nitrates. This increased the porosity of the sorbent and presumably allowed more of the dissolved nitrates to penetrate the particles. The nitrate-impregnated samples were

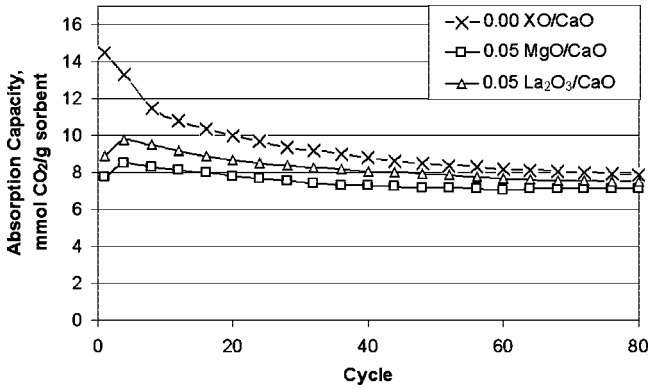

Figure 4. Comparison of effects of MgO and La_2O_3 expressed as g of XO/g of CaO on apparent absorption characteristics of CaO derived from Microna 3 limestone. The limestone was calcined at 750 °C for 5 h before adding $Mg(NO_3)_2$ or $La(NO_3)_3$. The mixture was then calcined at 900 °C for 3 h.

subsequently calcined at 900 °C for 3 h and then tested, which produced the results shown in Figure 4. A comparison of the results in Figure 4 with results presented in Figures 2 and 3 shows that the initial absorption capacity of the sorbents produced by the alternative method was less than that produced before. However, after 80 cycles the absorption capacities of the sorbents prepared by the alternative method were not significantly different from those prepared by the first method. On the other hand, the sorbents prepared by the alternative method were more stable, at least for 30 cycles.

The purpose of adding MgO to the Microna 3 limestone was to improve the stability of the sorbent by inhibiting sintering. SEM images were obtained of Mg-free samples and of samples with 0.05 g of MgO/g of CaO both before and after being subjected to a 30-cycle test. The samples were calcined initially at 900 °C for 3 h. Figure 5a is an image of the calcined limestone before testing, while Figure 5b is an image after testing. Although Figure 5a shows that the pure limestone experienced some sintering during initial calcination, it experienced more severe sintering during the 30-cycle test (Figure 5b). By comparison, the samples with MgO may have undergone slightly more sintering during initial calcination (Figure 5c) but much less sintering during the 30-cycle test (Figure 5d). Overall, it appeared that a small amount of MgO was beneficial.

The effects of initial calcination conditions on Microna 3 limestone prior to cyclic testing were also studied, and the results are shown in Figure 6. It was hypothesized that increasing the severity of the initial calcination conditions would produce larger pores in the mesoporous region, which would then allow CO_2

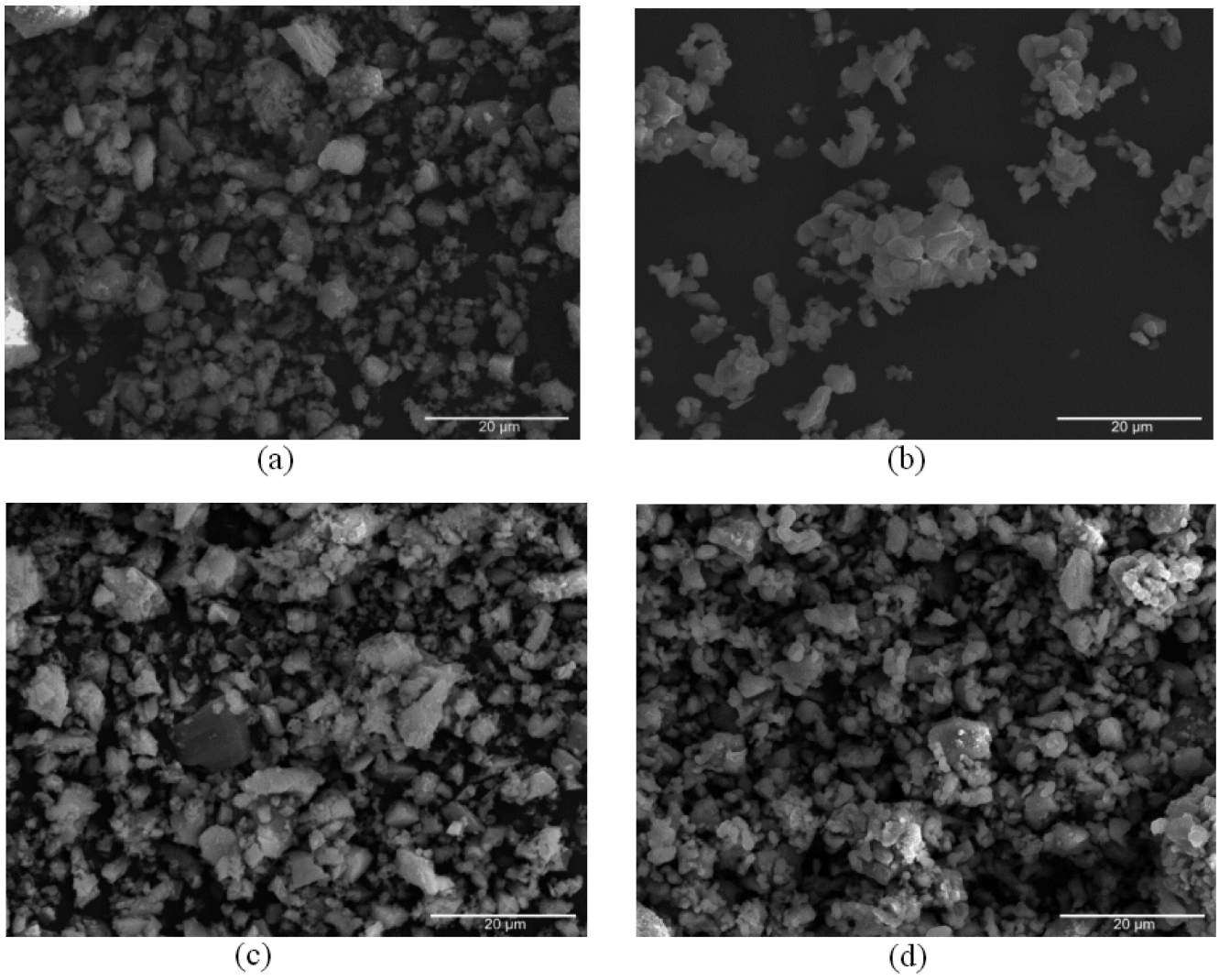

Figure 5. SEM micrographs of Microna 3 limestone samples after initial calcination at 900 °C for 3 h and after 30 cycles of CO_2 absorption and desorption at 750 °C. (a) After initial calcination without MgO; (b) after 30 cycles without MgO; (c) after initial calcination with 0.05 g of MgO/g of CaO; (d) after 30 cycles with 0.05 g of MgO/g of CaO.

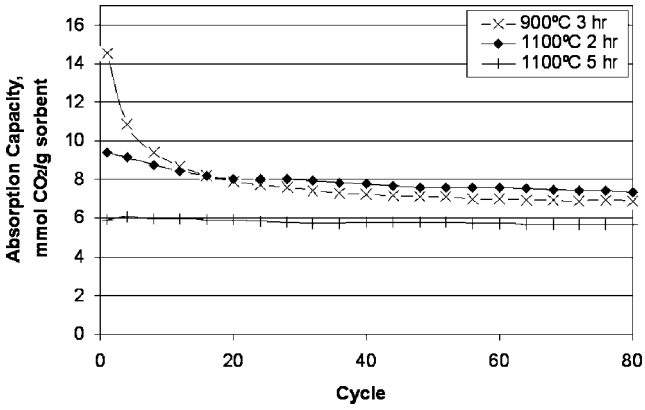

Figure 6. Effect of initial calcination conditions on apparent absorption capacity of CaO derived from Microna 3 limestone.

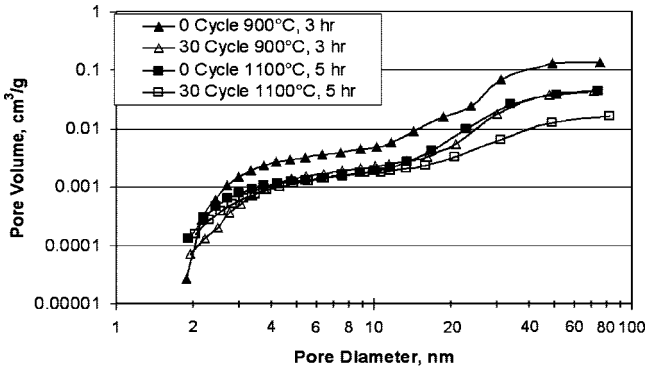

Figure 7. Cumulative pore volume distribution of Microna 3 limestone after it had been subjected to various treatments.

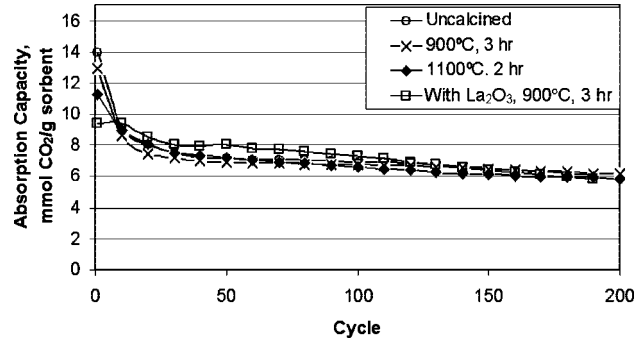

Figure 8. Various sorbents derived from Microna 3 limestone tested after being initially calcined at the indicated conditions. One sorbent contained 0.05 g of La_2O_3/g of CaO.

to penetrate deeper into a CaO particle because of reduced mass transfer limitations. However, this could also reduce the surface area available for sorption and reduce the absorption capacity. On the other hand, it could also result in a more stable material. Figure 6 shows that calcining the Microna 3 limestone at 1100 °C for 2 h produced a somewhat more stable sorbent than that produced by calcining the material at 900 °C for 3 h. Increasing the calcination time to 5 h while maintaining the 1100 °C temperature produced a more stable sorbent but with less capacity. Also, the sample that was calcined at 1100 °C for 5 h exhibited the interesting property of becoming slightly more active between the first and second cycles. This increase in activity may have been due to the development of new pores and cracks during the initial cycle of carbonation and regeneration of the CaO.

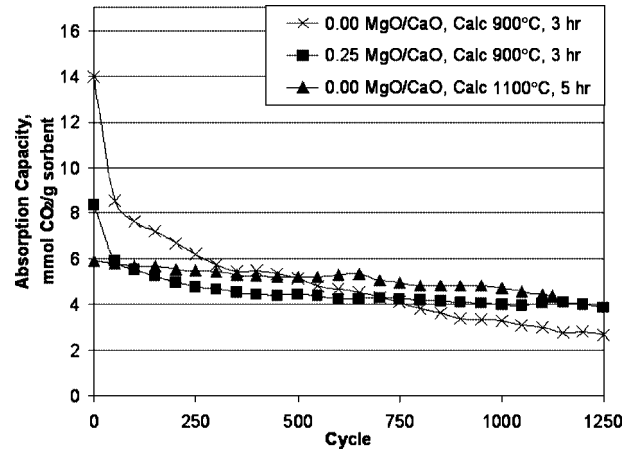

Figure 9. Absorption capacity of CaO derived from Microna 3 limestone. One sorbent contained 0.25 g of MgO/g of CaO. The sorbents had been initially calcined at either 900 °C for 3 h or 1100 °C for 5 h.

To provide greater insight into the effects of initial calcination conditions and repeated absorption and regeneration on the physical properties of the sorbent, samples of Microna 3 limestone were calcined initially at either 900 °C for 3 h or 1100 °C for 5 h and then subjected to a 30-cycle test of absorption and regeneration at 750 °C. The pore volume distribution of the samples was then determined after the initial calcination and after the 30-cycle test. Figure 7 shows on a logarithmic scale the cumulative pore volume of the samples that had received the different treatments. The sample calcined initially at 900 °C for 3 h had the largest cumulative pore volume, whereas the sample that had been calcined initially at 1100 °C for 5 h had less cumulative pore volume. Therefore, the more severe calcination conditions reduced both the pore volume and absorption capacity of the material, which was not desirable. However, these conditions did produce a more stable material. This increase in stability was reflected not only by the cyclic results in Figure 6 but also by the porosity results which are reported in Figure 7. The results of this test showed that after 30 absorption cycles the cumulative pore volume of the pores smaller than 10 nm was reduced only 6% for the sorbent calcined at 1100 °C for 5 h compared to a reduction of 54% for the sorbent calcined at 900 °C for 3 h.

Since it appeared that the life cycle performance of a sorbent could be better determined by extended testing, several sorbent samples were subjected to a 200-cycle test and three samples were even subjected to a test of 1100 cycles or more. The results are presented in Figures 8 and 9, respectively. In Figure 8, it can be seen that precalcining the sorbent had some effect initially, as did the calcination temperature. However, after 50−60 cycles there was little difference in the absorption capacity. It is also apparent that while a small amount of La_2O_3 was beneficial initially, any benefit disappeared after 120−130 cycles. These results again bring out the importance of extended life cycle testing of any proposed sorbent.

Further confirmation of this observation is provided by the results of the most prolonged testing presented in Figure 9. Two of the sorbents tested were based on Microna 3 limestone initially calcined at either 900 °C for 3 h or 1100 °C for 5 h. The third sorbent was composed of Microna 3 impregnated with $Mg(NO_3)_2$ to provide a material with 0.25 g of MgO/g of CaO after calcining at 900 °C for 3 h. The sorbents calcined at 900 °C for 3 h were tested for 1250 cycles, while the sample calcined at 1100 °C for 5 h was tested for 1124 cycles. The results presented in Figure 9 indicate that the absorption capacity of

the modified sorbents started with absorption capacities lower than that of the Microna 3 sample calcined at 900 °C for 3 h. However, as the number of cycles increased, the modified sorbents proved to be more stable than the Microna 3 sorbent calcined at 900 °C for 3 h. Consequently the absorption capacity of this material was surpassed by that of the material calcined at 1100 °C for 5 h after 500 cycles and by that of the sorbent with 0.25 g of MgO/g of CaO after 700 cycles. Whether a truly stable state had been achieved with the two modified sorbents could only have been determined by extending the test even further. Nevertheless, the results indicate that the modified sorbents were likely to retain their absorption capacity longer than the Microna 3 sample calcined at 900 °C for 3 h.

Another interesting result displayed by Figure 9 was the difference in absorption capacity of the CaO by the end of the test. At the end of the 1250-cycle test, the Microna 3 sample initially calcined at 900 °C for 3 h absorbed 2.68 mmol of CO_2/g of sorbent, which corresponded to a 15.8% conversion of CaO. However, the sorbent with 0.25 g of MgO/g of CaO absorbed 3.85 mmol of CO_2/g of sorbent, which corresponded to a 28.1% conversion of CaO. Thus, the presence of the inert MgO increased the absorption capacity of the CaO.

The results in Figure 9 are important because they show that the life cycle performance of the sorbent was improved significantly either by the addition of MgO or by the use of a higher initial calcination temperature.

Conclusions

The carbonation of CaO is an attractive method for removing CO_2 from hot gas mixtures such as are produced for example by steam reforming of methane. However, to be economical the sorbent must be regenerated and reused for many cycles, which requires maintaining the activity of the sorbent. A sorbent performance test of CaO derived from natural limestones and several pure materials showed that in every case the absorption capacity declined as the material was subjected repeatedly to a cycle of CO_2 absorption and regeneration. However, the rate of decline and the initial absorption capacity did vary somewhat depending on the source of the CaO such that CaO derived from pure calcium acetate had the highest absorption capacity after 30 cycles, and CaO derived from an Iowa limestone had the lowest.

Subsequent investigation showed that the rate of decline in CaO activity can be reduced by incorporating finely dispersed MgO in the sorbent. However, this also reduces the absorption capacity of the sorbent, since MgO does not absorb CO_2 under the proposed conditions of usage. Because of these competing effects, a long life cycle performance test was required to show the advantage of incorporating MgO in the sorbent. When such a test was conducted for 1250 cycles, the absorption capacity of a limestone-based sorbent with 20 wt % MgO was 45% greater than that of a similar material without MgO by the end of the test, and the rate of decline in absorption capacity was very small.

Further investigation showed that the stability of a CaO-based sorbent derived from limestone is also greatly affected by the initial calcinations conditions. Therefore, a material calcined at 1100 °C for 5 h is more stable than one calcined at 1100 °C for 2 h, which is more stable than one calcined at 900 °C for 3 h. Although the initial CO_2 absorption capacity of the material is inversely proportional to the severity of the calcination conditions, extended life cycle performance tests have shown that the material subjected to the more severe initial calcination condition can have the higher absorption capacity after many cycles. Consequently, the absorption capacity of a limestone sample calcined at 1100 °C for 5 h was 45% greater than that of a limestone sample calcined at 900 °C for 3 h by the end of a 1200-cycle test.

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